## Notes

The spectra of acetanilide and its titanium (IV) chloride complex also leave little doubt that coordination takes place through the carbonyl oxygen. A strong carbonyl absorption band at 1686 cm<sup>-1</sup> in the spectrum of the free amide in chloroform solution was shifted to 1612 cm<sup>-1</sup> in the spectrum of the complex in chloroform. Assuming this was the shifted carbonyl band, there was a shift of 74  $cm^{-1}$ to lower frequencies. A study of the spectra in the region in which N-H stretching bands appear, indicates some change. An absorption at  $3440 \text{ cm}^{-1}$  in the spectrum of the free amide completely disappears in the spectrum of the complex. This may be an indication that co-ordination also takes place through the nitrogen. The shifted band could be hidden by the strong chloroform absorption if the shift was about 400  $cm^{-1}$  to lower frequencies. The fact that the shift in the carbonyl absorption is nearly three times greater than for any of the other complexes may also be an indication of co-ordination through the nitrogen. Co-ordination through the nitrogen would eliminate the suggested electronic rearrangement discussed earlier in this section. The result of this should be a greater shift in the carbonyl band. Molecular weight data for the titanium (IV) chloride-acetanilide complex obtained on chloroform solutions indicates that the complex is essentially a monomer. Assuming that titanium maintains its usual co-ordination number of six, it becomes necessary for co-ordination to take place through both the oxygen and nitrogen. The structure, then, may be illustrated below:



Four-membered ring chelates such as this have been postulated for the complexes of titanium (IV) chloride with esters.<sup>(15)</sup>

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<sup>(15)</sup> E. RIVEST, R. AUBIN and R. RIVEST, Can. J. Chem. 39, 2343 (1961).

J. inorg. nucl. Chem., 1967, Vol. 29, pp. 1389 to 1391. Pergamon Press Ltd. Printed in Northern Ireland

## Substituted trinuclear ruthenium carbonyls

(Received 31 August 1966)

THE FIRST example of a phosphine derivative of ruthenium carbonyl,  $Ru(CO)_{s}[P(C_{s}H_{s})_{s}]_{s}$ , has been recently obtained<sup>(1)</sup> by reduction of  $RuCl_{s}(CO)_{s}[P(C_{s}H_{s})_{s}]_{s}$  in the presence of carbon monoxide.

We wish now to report that by reacting  $[Ru(CO)_4]_3$  in CH<sub>3</sub>OH or acetone solution at 55-60°C with P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, P(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> and P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (hereafter indicated as L) in the molar ratio of 1:4 a new series of ruthenium carbonyls is obtained where the Ru/L ratio is equal to 1 and the CO/Ru ratio is equal to 3; the molecular weight determinations carried out in benzene (Mechrolab Osmometer) on these compounds are in agreement with a  $[Ru(CO)_5L]_5$  formulation. By reacting  $[Ru(CO)_5P(C_6H_5)_3]_5$  or  $[Ru(CO)_5P(C_6H_5)_5]_5$  in methylethylketone solution at 130-140°C, under CO, with an excess of the corresponding ligand, complexes of the type  $Ru(CO)_5L_2$  are obtained. Elemental analyses and molecular weight determinations of all compounds prepared are reported in Table 1 (see p. 1390).

<sup>(1)</sup> J. COLLMAN and W. R. ROPER, J. Am. chem. Soc. 87, 4008 (1965).

|         | l.wt.<br>Calc. | 1344-0<br>1164-1<br>1488-0<br>709-7<br>594-4   |
|---------|----------------|--|
| TABLE 1 | Mo<br>Found    | 1403<br>1127<br>1542<br>725<br>603   |
|         | %<br>Calc.     | 22:7   |
|         | Ru<br>Found    | 21.8   |
|         | %<br>Calc.     | 6-91<br>7-98<br>6-25<br>10-49  |
|         | P,<br>Found    | 6:76<br>7-92<br>6:30<br>10:42  |
|         | %<br>Calc.     | 3·37<br>7·02<br>3·05<br>9·22   |
|         | Found          | 3-31<br>7-20<br>3-05<br>4-32<br>9-15   |
|         | %<br>Calc.     | 56·29<br>46·43<br>50·87<br>66·01<br>54·93  |
|         | Found          | 56-15<br>46-72<br>51-40<br>65-67<br>54-71  |
|         | M.P.<br>(°C)   | 174-176<br>62-63<br>77-78<br>250-251<br>42-43  |
|         | Colour         | dark violet<br>dark red<br>orange<br>yellow<br>pale yellow   |
|         |                | [Ru(CO) <sub>8</sub> P(C <sub>6</sub> H <sub>6</sub> ) <sub>3</sub> ] <sub>5</sub><br>[Ru(CO) <sub>8</sub> P(C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> ] <sub>5</sub><br>[Ru(CO) <sub>8</sub> P(OC <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> ] <sub>5</sub><br>Ru(CO) <sub>8</sub> [C <sub>6</sub> H <sub>8</sub> ) <sub>4</sub> ] <sub>5</sub> <sup>4</sup><br>Ru(CO) <sub>3</sub> [P(C <sub>4</sub> H <sub>6</sub> ) <sub>5</sub> ] <sub>5</sub> |

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| Compound                             | Medium                          | CO stretching (cm <sup>-1</sup> )* |        |         |         |
|--------------------------------------|---------------------------------|------------------------------------|--------|---------|---------|
| $Ru(CO)_{3}[P(C_{6}H_{5})_{3}]_{2}$  | nujol                           | 1903 s                             |        | 1895 s  |         |
|                                      | CH <sub>2</sub> Cl <sub>2</sub> |                                    |        | 1895 s  |         |
| $Ru(CO)_{3}[P(C_{4}H_{9})_{3}]_{2}$  | nujol                           | 1884 s                             |        | 1878 s  |         |
|                                      | CH <sub>2</sub> Cl <sub>2</sub> |                                    |        | 1876 s  |         |
| $[Ru(CO)_{3}P(C_{6}H_{5})_{3}]_{3}$  | nujol                           | 1982 s                             | 1969 s | 1935 s  |         |
|                                      | CH <sub>2</sub> Cl <sub>2</sub> | 1980 s                             | 1969 s | 1945 sh |         |
| $[Ru(CO)_{3}P(C_{4}H_{9})_{3}]_{3}$  | nujol                           | 2035 w                             | 1964 s | 1930 m  |         |
|                                      | CH <sub>2</sub> Cl <sub>2</sub> | 2035 vw                            | 1960 s | 1927 sh |         |
| $[Ru(CO)_{3}P(OC_{6}H_{5})_{3}]_{3}$ | nujol                           | 2001 s                             | 1985 s | 1970 m  | 1945 sł |

TABLE 2

\* A 221 Model Perkin-Elmer spectrophotometer with prism-grating interchange was used.

The i.r. spectra in the C=O stretching region (Table 2) of the trimeric species are more complex than those of the monomeric one. For  $Ru(CO)_{s}[P(C_{6}H_{5})_{s}]_{2}$  in  $CH_{s}Cl_{2}$  one band at 1895 cm<sup>-1</sup> is found in agreement with COLLMAN and ROPER;<sup>(1)</sup> in nujol paste two strong bands at 1903 and 1895 cm<sup>-1</sup> are present.

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